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Final Technical Report No 1

## A Kinetic Study of Hydrocarbon-Oxygen-Nitrogen Flames

A. VAN TIGGELEN

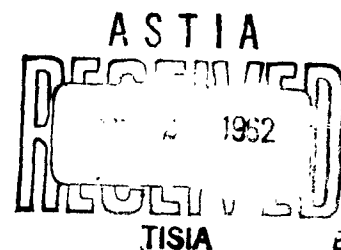
Professor at the University of Louvain (Belgium)

with the collaboration of

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holder of a NATO Science Fellowship

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Laboratory for Inorganic Chemistry

UNIVERSITY OF LOUVAIN

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# A KINETIC STUDY OF HYDROCARBON-OXYGEN-NITROGEN FLAMES

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## INTRODUCTION

The complexity of most theories which attempt to correlate the basic principles of flame propagation restricts their practical application to the simplest systems. A general but very simple theory of stationary premixed flames has been developed in this laboratory<sup>1,2</sup>. It proposes that reaction is sustained by active centers which diffuse, against the gas flow, from the burned gas into the reaction zone. Chain branching compensates for radicals which are lost through terminating reactions, or by being swept away with the burned gases. A simple expression for the propagation of the combustion wave into the unburned gas is obtained from an analysis of this branched chain mechanism. The justification for this simplified approach lies in the ability of the theory to correlate all the experimental data relating to the different flame properties.

The burning velocity,  $V_o$ , relative to the unburned gases at the temperature,  $T_o$ , at which gas flows are measured (room temperature), can be expressed as

$$V_o = \frac{4T_o}{\pi} \left[ \frac{2R}{3T_m M} \right]^{\frac{1}{2}} \left[ \frac{(A)^a (B)^b}{P^i} e^{-\frac{E}{RT_m}} \right]^{\frac{1}{2}} \quad (1)$$

where  $P$  is the total pressure,  $(A)$  and  $(B)$  are the partial pressures of oxidant and fuel, respectively,  $R$  is the gas constant,  $M$  is the mean molecular weight of the chain carrying species, and  $E$  is an overall activation energy.  $T_m$  is the mean flame temperature for which the following relation has been proposed<sup>1</sup> as a first approximation :

$$T_m = T_i + 0.74 (T_f - T_i) \quad (2)$$

where  $T_i$  and  $T_f$  are, respectively, the initial temperature of the unburned gas, and the maximum flame temperature. Exponents  $\underline{a}$  and  $\underline{b}$  are the partial orders with respect to oxidant and fuel; their sum  $a + b = i$ , has been found to be unity for all flames studied to date<sup>2, 3, 4</sup>, except those of hydrogen<sup>5</sup>. Since the branching reaction is also first order with respect to radical concentration, the global order is  $i + 1$ ; that is, two for the majority of flames.

An activation energy can be determined by observing the change in burning velocity with temperature keeping all other parameters, notably concentration and pressure, constant. Thus if equation (1) in a logarithmic form,

$$\log V_o + 1/2 \log T_m = \text{constant} - E \frac{\log e}{2RT_m} \quad (3)$$

is applied to a series of flames with a given mixture composition and pressure but burning at different temperatures, a plot of  $\log V_o + 1/2 \log T_m$  against  $1/T_m$  will give the overall activation energy  $E$  of flame propagation. This activation energy will be principally that of the chain branching process, with smaller contributions from the propagating reactions. Such a series of experiments can be effected by preheating the gases which feed the burner. However, as the preheating temperature must not exceed that at which slow reaction begins, this method is at times restricted to a prohibitively small temperature range.

Equation (1) may be written as follows :

$$V_o = \frac{K_o T_o}{T_m^{1/2}} \left[ \frac{(A)^a (B)^b}{[(A) + (B)]^i} \cdot Y^i \cdot e^{\frac{-E}{RT_m}} \right]^{1/2}$$

where  $Y = \frac{(A) + (B)}{P}$ ; that is,  $Y$  is the fraction of flammable mixture in the total gas volume. Then, if the logarithmic form of this equation

$$\log V_o + 1/2 \log T_m - i/2 \log Y = \text{constant} - E \frac{\log e}{2RT_m} \quad (5)$$

is applied to a series of flames with a constant oxidant-fuel ratio, burning at constant pressure, but with  $T_m$  varied by changing the value of  $Y$ ,  $E$  can be obtained by plotting the L.H.S. against  $1/T_m$ . The changes in  $Y$  are achieved by adding increasing amounts of an inert gas ( $N_2$ ). This method makes a wide temperature range available for study, but requires the a priori knowledge of the global order of reaction. Fortunately, this can be deduced from a theoretical consideration of the branching mechanism. Excellent agreement has been found between these two methods for determining activation energies.

The partial orders with respect to oxidant and fuel,  $\underline{a}$  and  $b$ , are not necessarily constant if the composition of the burning mixture is varied between wide limits, but the sum remains constant and equal to 1. The variation of  $\underline{a}$  and  $\underline{b}$  when the fuel to oxidant ratio is modified can be shown from an analysis of flame velocities and temperatures if the activation energy is known from one of the methods described above. Equation (1) can be rearranged in the following form .

$$\frac{V_o T_m^{1/2}}{K_o T_o} \left[ e^{E/RT_m} \right]^{1/2} = \left[ \frac{(A)^a (B)^b}{P^{a+b}} \right]^{1/2} \quad (6)$$

Since  $a + b = 1$ , equation (6) can be transformed into the logarithmic form :

$$2 \log V_o + \log T_m + 0.4343 E/RT_m - 1 \log [(B)/P] = 2 \log K_o T_o + a \log [(A)/(B)] \quad (7)$$

A plot of the L. H. S. of equation (7) against  $\log [(A)/(B)]$  gives a curve, the slope of which at any point gives the partial order  $\underline{a}$  with respect to oxidant for the particular composition  $(A)/(B)$ . The corresponding order  $\underline{b}$  with respect to fuel is obtained by subtracting  $\underline{a}$  from 1.

The chain is propagated by two radicals;  $X$ , which is formed

from the fuel, B, and reacts with the oxidant, A; and Y, which is formed from a reaction with a fuel molecule, and in turn reacts with the oxidant. The mean molecular weight of the chain-carriers M can be defined as follows :

$$M = \frac{M_x \tau_x + M_y \tau_y}{\tau} \quad (8)$$

where  $\tau_x$  and  $\tau_y$  are the mean lifetimes of radicals X and Y;

$\tau = \tau_x + \tau_y$  and is the total duration of one complete chain link;

$M_x$  and  $M_y$  are the actual molecular weights of radicals X and Y. The mean molecular weight can be calculated from the following equation<sup>2</sup>:

$$\frac{V_0}{\sqrt{T_m}} = \frac{3.9 \times 10^{-2}}{\sqrt{M}} \cdot \frac{1}{X_0} \quad (9)$$

if the mean free path of the chain carriers under standard conditions is accepted as  $10^{-5}$  cm. Here  $X_0$  is the flame front thickness, which has been demonstrated experimentally to obey the following relationship<sup>5</sup>,

$$S = 4.7 X_0$$

where S is the distance between the luminous and the schlieren cones of a flame. Thus M can be determined from a knowledge of  $V_0$ ,  $T_m$  and S, all of which are experimentally determinable.

Flames propagating in mixtures of oxygen with such hydrogen containing fuels as hydrogen itself, acetylene, methane, ethylene, ethane, propane, benzene, carbon monoxide contaminated with hydrogen, diethylether, and ammonia have been found to have a nearly common value for M. This is expected if . (a)  $M_x$  and  $M_y$  are almost equal, e. g. such pairs as  $\text{CH}_3$ . and  $\text{OH}$ ., or  $\text{NH}_2$ . and  $\text{OH}$ ., or (b) one chain propagating radical has a much longer lifetime than the other (e. g. if  $\tau_y \gg \tau_x$ , which implies that rate  $(X + A) \gg \text{rate } (Y + B)$ ). The variety of fuels giving a single value for M suggests that one, at least, of the chain carriers is the same in each case. The chain carrier is most probably the



radical OH, with  $M = 17$ . Its lifetime,  $\tau_{OH}$ , would be expected, theoretically, to be greater than  $\tau_x$ , because a hydrogen abstraction by OH from a hydrocarbon<sup>7</sup> for example, will have an activation of 6-8 Kcal mole<sup>-1</sup>; whereas that for reaction of the resultant alkyl radical with oxygen<sup>8</sup> is unlikely to be greater than 0-1 kcal mole<sup>-1</sup>. Furthermore, the two examples in case (a) for ammonia and methane flames will give a value of  $M$  near to 17 for all ratios of  $\tau_x$  to  $\tau_y$ .

However, the tested hydrocarbons are such that they have either low molecular weights and/or strong C-H bonds, which properties would, if OH is to be accepted as one chain carrier, tend to lower the molecular weight of its alternate and/or reduce  $\tau_x$ ; both trends lead to values of  $M$  which will be experimentally indistinguishable from one hydrocarbon to another.

Isobutane has been selected for the present investigation because its corresponding alkyl radical has a molecular weight 3.3 times that of OH, and furthermore because the weaker tertiary C-H bond should give rise to a more stable alkyl radical than in previous cases. An augmented value for  $M$  might thus be found, if alkyl radicals are chain carriers complementary to OH in the flames. Also, these same properties might exert some influence on the activation energy of the branching process.

For comparison, and to distinguish between the effects of molecular size and of C-H bond strength, neopentane, containing only primary bonds, has also been investigated. The system n-butane-oxygen was chosen to complete the study because those effects attributable to bond strength should lie between the extremes found for isobutane and neopentane for such a substance which contains secondary C-H bonds.

Burning velocities, flame temperatures and the distances between schlieren and luminous cones have therefore been determined for iso-butane-oxygen mixtures, neopentane-oxygen mixtures, and n-butane-oxygen mixtures, all diluted with nitrogen, and the experimental results and their implications are presented in the following sections.

## EXPERIMENTAL

Photographic images of the schlieren and luminous flames cones of approximately equal intensity were obtained as described previously<sup>6</sup>. Flame velocities were determined by the total area method applied to the outside edge of the schlieren cone for those flames in which the schlieren and luminous cones were distinguishable. At preheating temperature above about 500 °K; the previously observed coalescence of schlieren and luminous images<sup>4</sup> necessitated the calculation of flame velocities from the inner edge of the luminous cone. The surface of the cones was calculated from tenfold enlargements of the photographic images. Each velocity is the mean of three measurements, reproducible to within  $\pm 2\%$ .

The method of measurement of the distance between the schlieren and luminous cones is described in reference 6. Each distance reported is the mean of twelve measurements, four made on each of three films; reproducibility is  $\pm 5\%$ .

For unpreheated mixtures, 5 mm diameter waterjacketed conical burners, 100 cm in length, produced flames whose schlieren images approached perfect right cones. Preheating of the mixture by the burning flame did not exceed 5°.

When the gases were to be preheated, isobutane and nitrogen were entrained together and passed through a 300 cm length of 4 mm stainless steel tube, wound in a spiral around a 60 cm length of 10 mm diameter steel tube. Oxygen passed through a similar spiraled tube, and all gases entered the central tube at its base. The central tube, which was long enough to insure thorough mixing and a laminar gas flow at the flow rates used, was fitted with a 5 mm diameter burner head to give a conical flame. An insulated heating coil was wound outside the two spirals, and the whole was insulated with asbestos to reduce heat loss to the atmosphere. By maintaining a constant current input to the heating coil, exit gas temperatures could be held constant to  $\pm 2^\circ$  for an indefinite period.

The preheating temperature was measured immediately upon extinguishing a flame, after each series of photographs, with a single junction iron-constantan thermocouple inserted to a depth of 1 mm along the burner axis. No evidence of erroneously high temperatures due to catalytic effects on the thermocouple surface was found. At the maximum preheating temperatures, 635° K for isobutane mixtures, and 560° K for neopentane mixtures, neither carbon dioxide nor formaldehyde could be detected in the unignited gas stream. Mixtures containing n-butane were not preheated.

Flame temperatures were measured by the sodium line reversal method<sup>6</sup>. Flames were uniformly colored by heating a sodium borate bead formed on a small resistance coil placed in the nitrogen stream. The calibrated tungsten ribbon lamp was frequently checked against standard methane-oxygen-nitrogen flames, to detect possible disalignment of the optical system, or drifts in the lamp. Reproducibility of temperature measurement is  $\pm 10^\circ$ .

All gases were commercial grade, purity about 99 %. Trace impurities cause negligible errors, as it has been shown<sup>9</sup> that changes in velocity and temperature, when a second fuel is added to a flammable mixture, are small, and as a first approximation, may be taken as a linear extrapolation of the values for the separate fuels.

Gas flows were measured against a constant counter pressure of 6 cm Hg, to compensate for any resistance in the preheating tubes or in the burner itself. Hydrocarbon flow rates were measured on capillary flow meters; oxygen and nitrogen flows on rotameters. The flowmeters were calibrated at frequent intervals against a standard wet testmeter.

## RESULTS

### 1. The Isobutane-oxygen-nitrogen system

#### a. Preheated mixtures

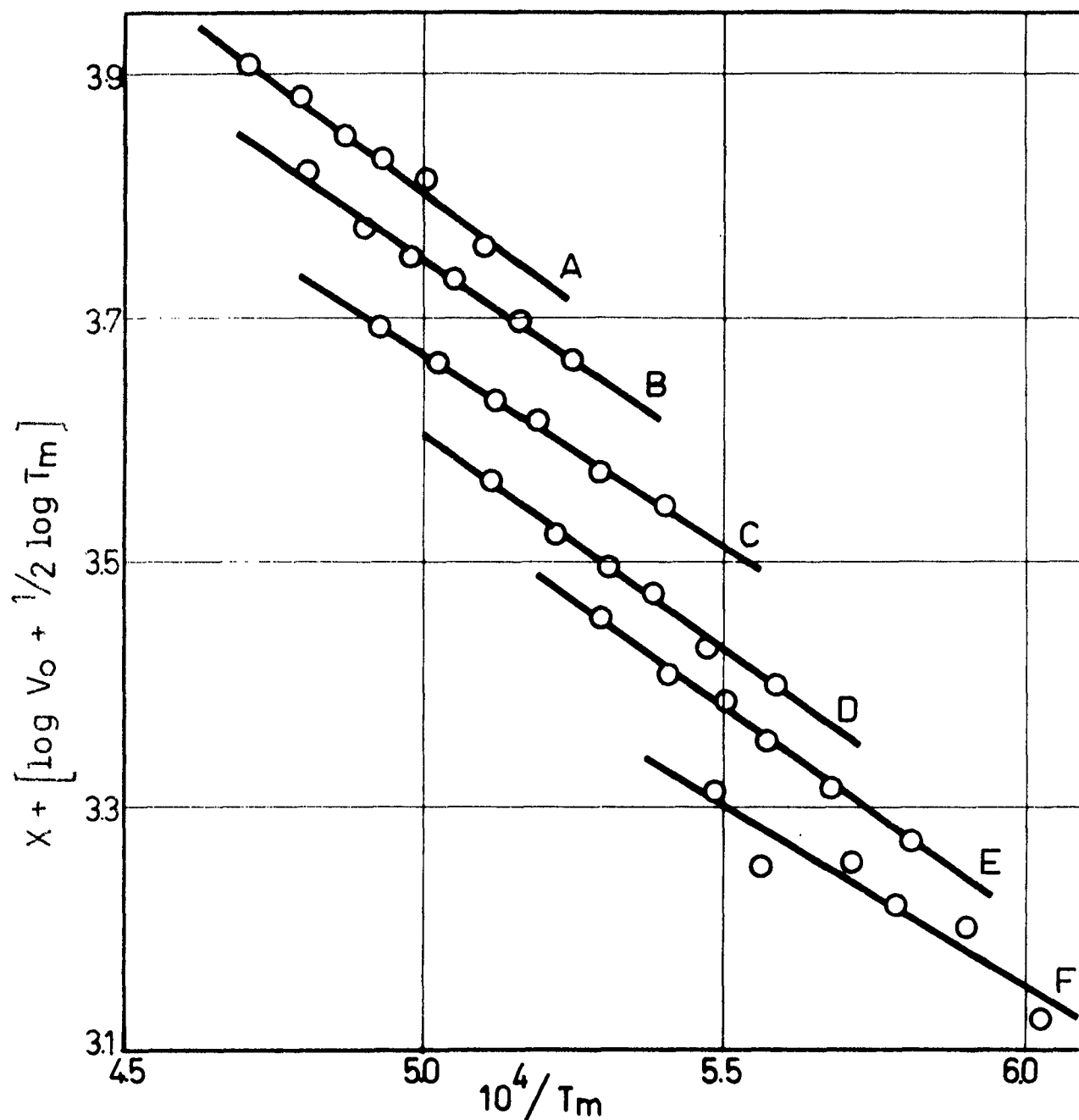
Flame velocities and temperatures of six mixtures where  $R = \frac{(\text{iso C}_4\text{H}_{10})}{(\text{iso C}_4\text{H}_{10}) + (\text{O}_2)} = 0.130$ , and the nitrogen content varied from 66 to 75 percent, were measured over an initial temperature range of 300° to 635° K. Straight lines are obtained if the experimental values of  $T_f$ ,  $T_m$  and  $V_o$  (presented in Table 1) are plotted against the initial temperature,  $T_1$ .

An activation energy of  $30.0 \pm 1.6 \text{ kcal mole}^{-1}$  is found by plotting these data in accordance with equation (3), as has been done in Figure 1. When the data for mixtures diluted with 66 to 73 percent nitrogen are plotted in accordance with equation (5), a single line is found whose slope corresponds to an activation energy of  $31.0 \text{ Kcal mole}^{-1}$  (Figure 2A). The inclusion of the more erratic data for slow propagation flames with 75 percent nitrogen in the plot would increase this value by about  $1 \text{ kcal mole}^{-1}$ .

#### b. Unpreheated mixtures :

The results from experiments with unpreheated isobutane-oxygen mixtures are reported in Table 2. For six fuel-oxidant ratios, the dilution by nitrogen was varied over as wide a range as was practicable. The minimum nitrogen content was dictated by the maximum temperature that could be measured by the sodium line reversal apparatus; the maximum dilution was that which still permitted the stabilisation of conical flames on the burner.

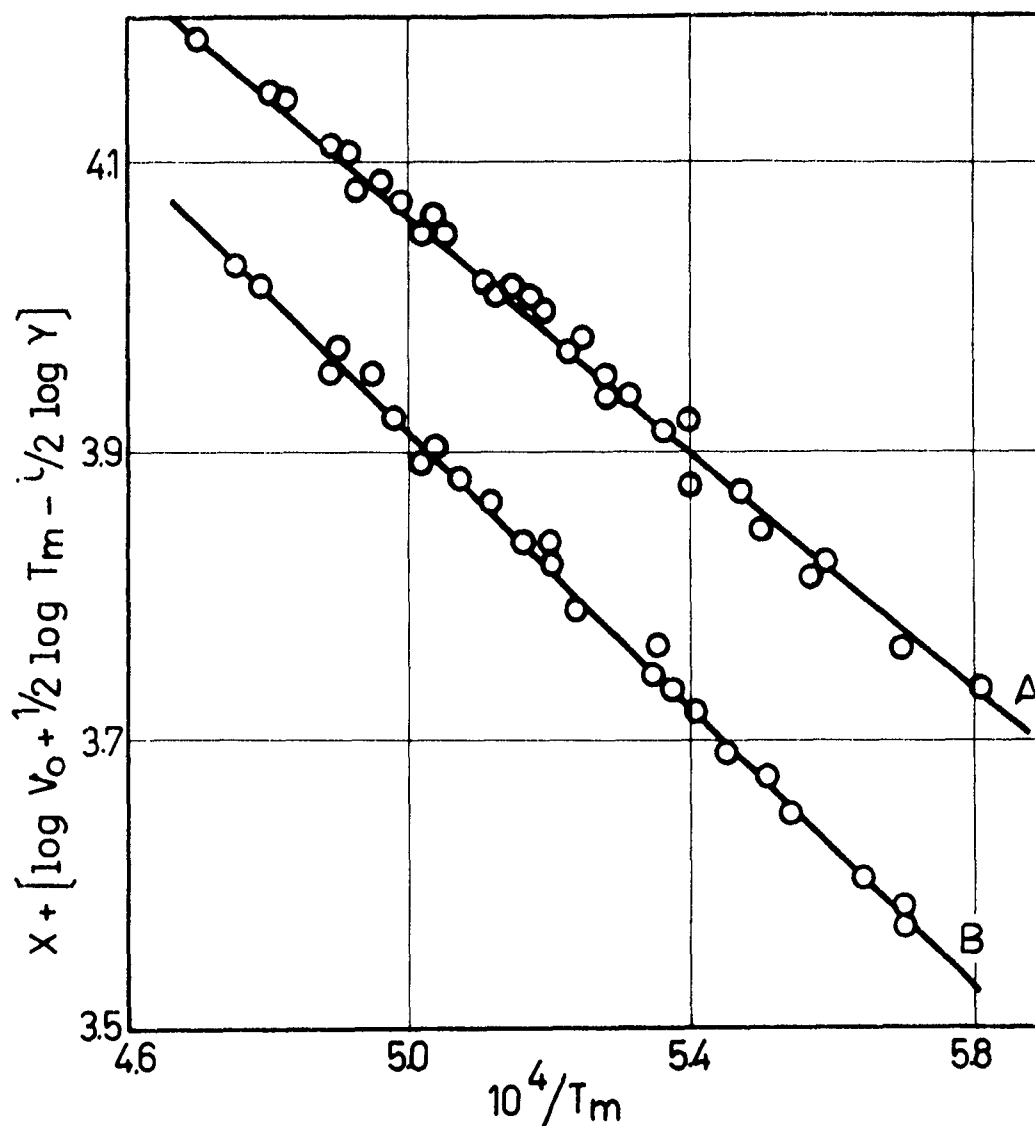
Plots of flame velocity,  $V_o$ , and the reciprocal of the intercone distance,  $1/s$ , against the fraction of flammable mixture,  $Y$ , are straight lines within the experimental accuracy; plots of mean flame temperature,



ACTIVATION ENERGY OF ISOBUTANE-OXYGEN FLAMES  
FROM PREHEATING DATA

A: $X=0.15$ , $E=31.3$ , $N_2=66\%$	B: $X=0.10$ , $E=30.4$ , $N_2=71\%$
C: $X=0.05$ , $E=27.7$ , $N_2=67\%$	D: $X=0$ , $E=32.1$ , $N_2=73\%$
E: $X=0$ , $E=31.2$ , $N_2=69\%$	F: $X=0$ , $E=27.5$ , $N_2=75\%$

FIGURE 1.



ACTIVATION ENERGIES FROM PREHEATING DATA  
USING DILUTION METHOD OF CALCULATION

A: ISOBUTANE-OXYGEN FLAMES,  $X=0.1$ ,  $E=31.0$

B: NEOPENTANE-OXYGEN FLAMES  $X=0$ ,  $E=36.7$

FIGURE 2

TABLE 1

PREHEATED ISOBUTANE-OXYGEN-NITROGEN FLAMES; R = 0.130

$N_2$ %	$T_i$ °K	$T_f$ °K	$T_m$ °K	$V_o$ cm/sec
66	300	2535	1954	90
	360	2564	1991	100
	426	2585	2024	104
	469	2600	2046	108
	531	2625	2080	114
	636	2650	2126	120
67	300	2473	1908	85
	360	2492	1938	90
	424	2530	1982	96
	464	2552	2009	99
	528	2572	2041	105
	625	2590	2079	114
69	300	2397	1852	73
	361	2430	1892	77
	424	2457	1928	84
	466	2474	1952	87
	530	2506	1992	92
	623	2526	2031	97
71	303	2313	1790	59
	360	2345	1829	63
	422	2362	1858	69
	464	2378	1883	72
	528	2402	1915	76
	608	2430	1956	83
73	303	2219	1721	45
	361	2254	1762	49
	421	2278	1795	53
	465	2293	1818	57
	525	2317	1851	59
	599	2341	1888	65
75	300	2134	1657	33
	359	2165	1695	38
	417	2190	1729	41
	459	2208	1753	43
	512	2234	1786	45
	586	2260	1825	48

TABLE 2

UNPREHEATED ISOBUTANE-OXYGEN-NITROGEN FLAMES

R	N <sub>2</sub> %	T <sub>f</sub> °K	T <sub>m</sub> °K	V <sub>o</sub> cm/sec	S cm x 10 <sup>2</sup>
0.140	57.5	2718	2086	128	1.42
	60.7	2668	2049	110	1.54
	62.5	2620	2014	103	1.74
	65.0	2545	1958	96	1.91
	67.5	2454	1891	81	2.31
	70.0	2357	1819	69	2.34
	72.5	2240	1733	52	2.80
	75.0	2117	1642	38	3.62
	77.5	1980	1540	22	5.57
0.133	57.5	2775	2120	126	1.34
	60.0	2728	2090	115	1.49
	62.5	2660	2040	108	1.69
	65.0	2568	1975	94	2.00
	67.5	2475	1905	82	2.08
	70.0	2372	1825	68	2.46
	72.5	2260	1745	50	2.98
	75.0	2132	1650	37	3.91
	77.5	1995	1550	26	5.00
0.130	57.5	2723	2090	126	1.30
	60.7	2672	2052	110	1.42
	62.5	2620	2014	108	1.55
	65.0	2550	1962	95	1.80
	67.5	2465	1899	83	2.24
	70.0	2367	1827	71	2.25
	72.5	2262	1749	53	2.72
	75.0	2130	1651	39	3.56
	77.5	2005	1559	29	4.04
0.120	55.0	2740	2103	139	1.27
	57.5	2733	2095	123	1.26
	60.0	2647	2034	114	1.53
	62.5	2610	2005	102	1.68
	65.0	2532	1945	90	1.80
	67.5	2445	1880	80	2.00
	70.0	2360	1820	67	2.29
	72.5	2247	1735	53	2.62
	75.0	2147	1660	43	3.09
	77.5	2000	1550	29	4.17



TABLE 2 (continued)

UNPREHEATED ISOBUTANE-OXYGEN-NITROGEN FLAMES

R	N <sub>2</sub> %	T <sub>f</sub> °K	T <sub>m</sub> °K	V <sub>o</sub> cm/sec	S cm x 10 <sup>2</sup>
0.110	52.5	2713	2083	145	1.15
	55.0	2707	2078	137	1.21
	57.5	2657	2042	122	1.35
	60.0	2603	2000	111	1.47
	62.5	2567	1975	100	1.62
	65.0	2480	1910	89	1.88
	67.5	2392	1840	72	2.11
	70.0	2297	1770	63	2.32
	72.5	2215	1710	52	2.90
	75.0	2100	1625	43	3.19
	77.5	1968	1530	29	4.30
	50.0	2730	2097	151	0.97
	52.5	2693	2070	138	1.16
	55.0	2685	2060	123	-
0.100	57.5	2609	2008	110	1.49
	60.0	2570	1975	104	1.49
	62.5	2500	1920	94	1.60
	65.0	2413	1860	79	1.91
	67.5	2335	1800	71	2.12
	70.0	2235	1730	60	2.43
	72.5	2152	1665	48	3.09
	75.0	2055	1595	38	3.44
	77.5	1905	1480	27	4.69

$T_m$ , against  $Y$  are curved towards the concentration axis.

It is noteworthy that for mixtures burning with constant dilution, but with

$$R = \frac{(\text{iso } C_4H_{10})}{(\text{iso } C_4H_{10}) + (O_2)}$$

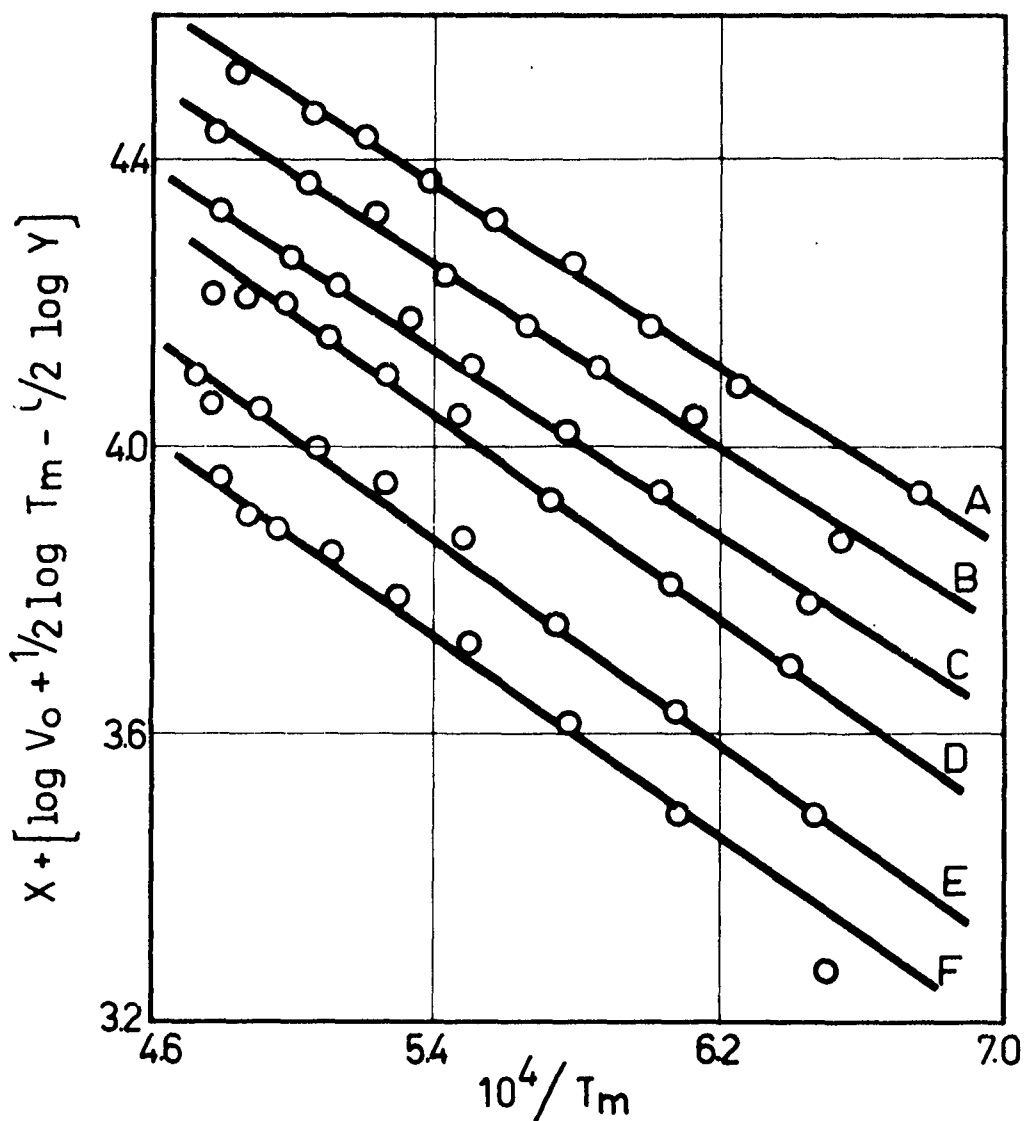
varied between 0.100 and 0.140, that the maximum of flame temperature and velocity shift towards lean mixtures when the dilution increases. This behavior has also been observed for  $H_2S$  flames burning in oxygen<sup>10</sup>, but is in opposite to the normal drift for fuel-oxygen-systems.

An activation energy of  $30.7 \pm 1.2$  kcal mole<sup>-1</sup> is found when the data in Table 2 are plotted as in Figure 3.

A plot of  $V_o / \sqrt{T_m}$  against  $1/S$  for the six values of  $R$  studied, (Figure 4) gives a single straight line whose slope yields a value of 24 for the mean molecular weight  $M$  of the chain carrying species. Lean mixtures tend to give a slightly higher value for  $M$  than stoichiometric or rich mixtures, but the difference is less than the experimental deviation, and it is doubtful if any significance can be assigned to this trend.

In Figure 5, the L.H.S. of equation (7) is plotted against  $\log [(O_2)/(\text{iso } C_4H_{10})]$ . In calculating these points,  $i$  was assumed to be unity, and a mean value of  $30.5$  kcal mole<sup>-1</sup> was taken for the activation energy. Each point is the mean of between 30 and 40 measurements; the vertical lines indicate the mean deviation from the plotted values.

From the slope of this line, the partial order,  $a$ , with respect to oxygen is found to be constant, and equal to 1.5. Since  $i$  is unity, the partial order,  $b$ , with respect to fuel is also a constant,  $\approx 0.5$ , over the concentration range investigated.



ACTIVATION ENERGY OF ISOBUTANE-OXYGEN  
FLAMES FROM DILUTION DATA ;  $\bar{L} = 1$

A: $X = 0.6$ , $R = 0.100$ , $E = 29.6$	B: $X = 0.5$ , $R = 0.110$ , $E = 29.3$
C: $X = 0.4$ , $R = 0.120$ , $E = 29.7$	D: $X = 0.3$ , $R = 0.130$ , $E = 31.7$
E: $X = 0.15$ , $R = 0.133$ , $E = 32.6$	F: $X = 0$ , $R = 0.140$ , $E = 31.5$

FIGURE 3

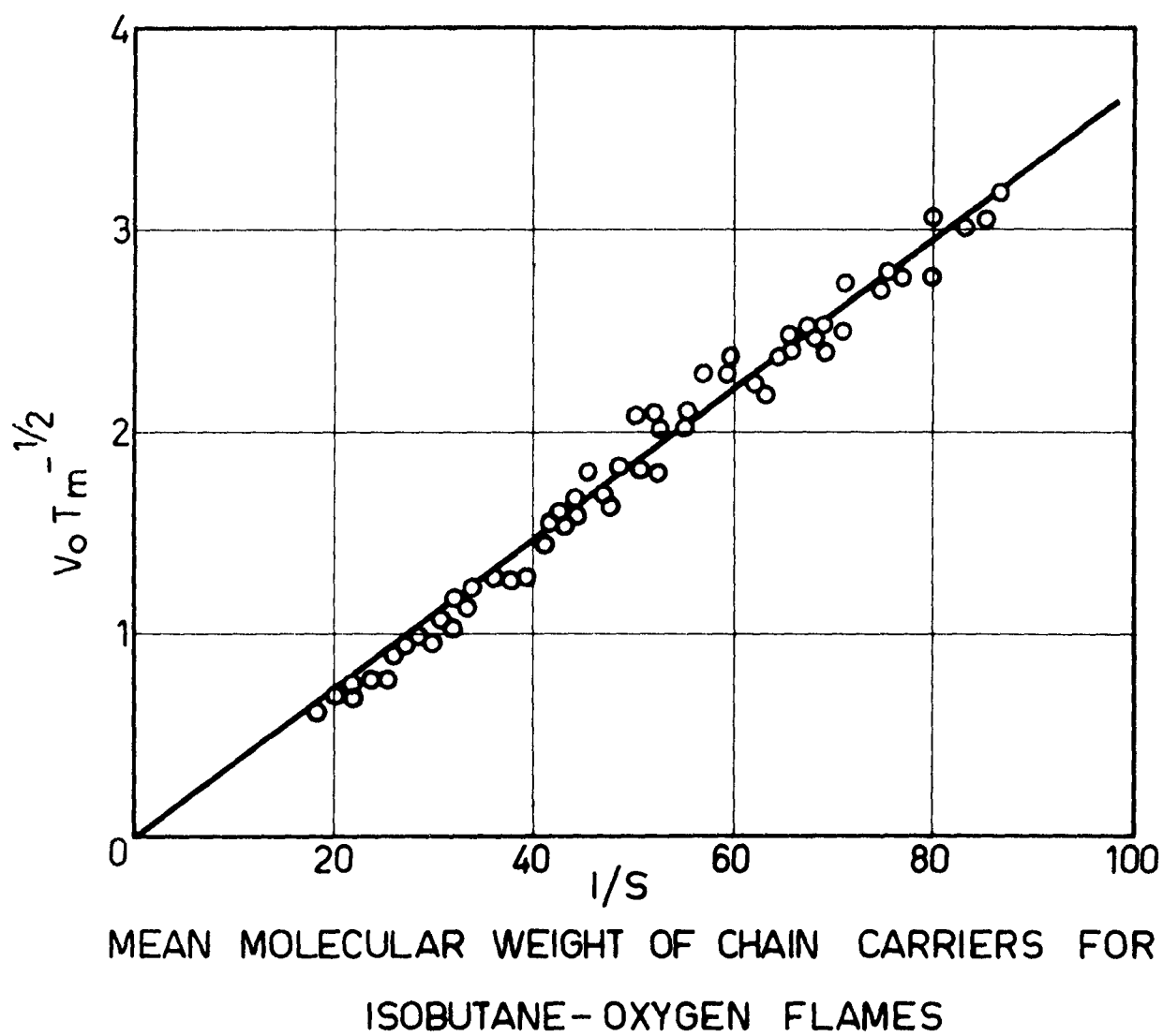
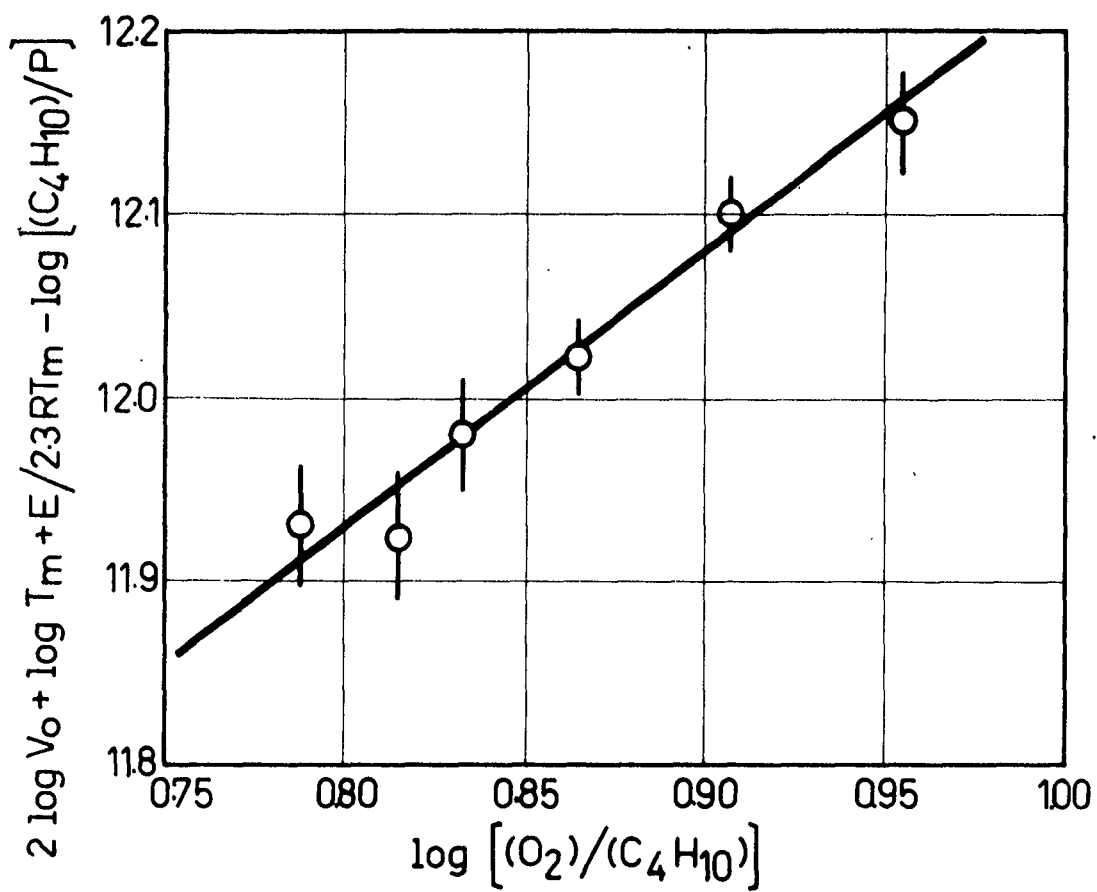


FIGURE 4.



ORDER OF THE BRANCHING REACTION WITH RESPECT  
TO OXYGEN FOR ISOBUTANE-OXYGEN FLAMES

FIGURE 5

## 2. The neopentane-oxygen-nitrogen system

### a. Preheated mixtures :

Flame velocities, temperatures, and if possible, the distances between the luminous and schlieren cones for five mixtures, where

$$R = \frac{(\text{neo C}_5\text{H}_{12})}{(\text{neo C}_5\text{H}_{12}) + (\text{O}_2)} = 0.111$$

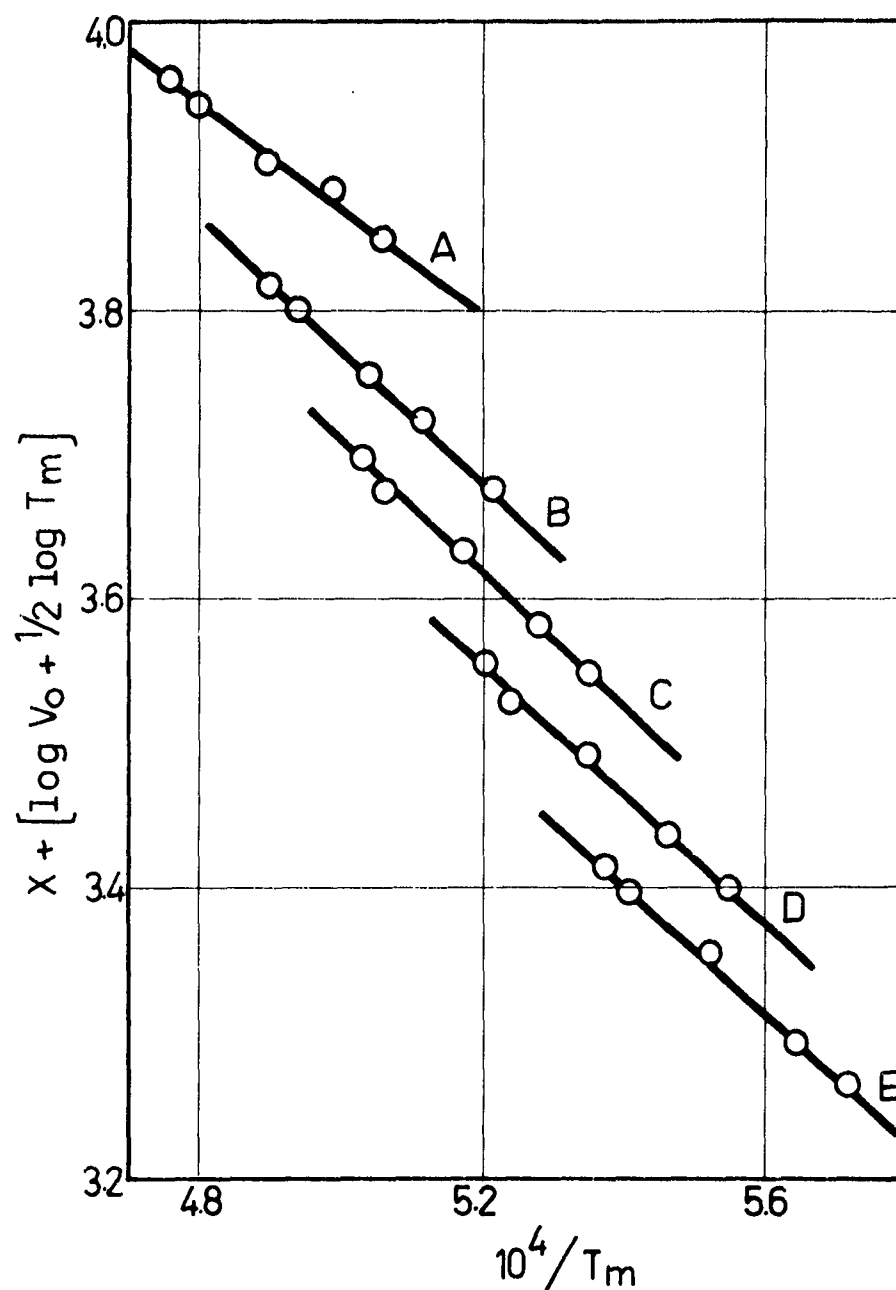
and the nitrogen content varied from 65 to 73 percent, were measured over an initial temperature range of 300° to 560°K. Straight lines are obtained if the experimental values of  $T_f$ ,  $T_m$  and  $V_o$  (presented in Table 3) are plotted against  $T_1$ .

An activation energy of  $39.3 \pm 1.1$  kcal mole<sup>-1</sup> is found by plotting these data in accordance with equation (3), as has been done in Figure 6. If these data are plotted in accordance with equation (5), a single line is found whose slope corresponds to an activation energy of 36.7 kcal mole<sup>-1</sup> (Figure 2B).

A plot of  $V_o / \sqrt{T_m}$  against  $1/S$  has been made in Figure 7 using the data for those preheated mixtures in which  $S$  was measured combined with the data from unpreheated mixtures. A single straight line whose slope yields a value of 28 for the mean molecular weight of the chain carrying species is obtained.

### b. Unpreheated mixtures :

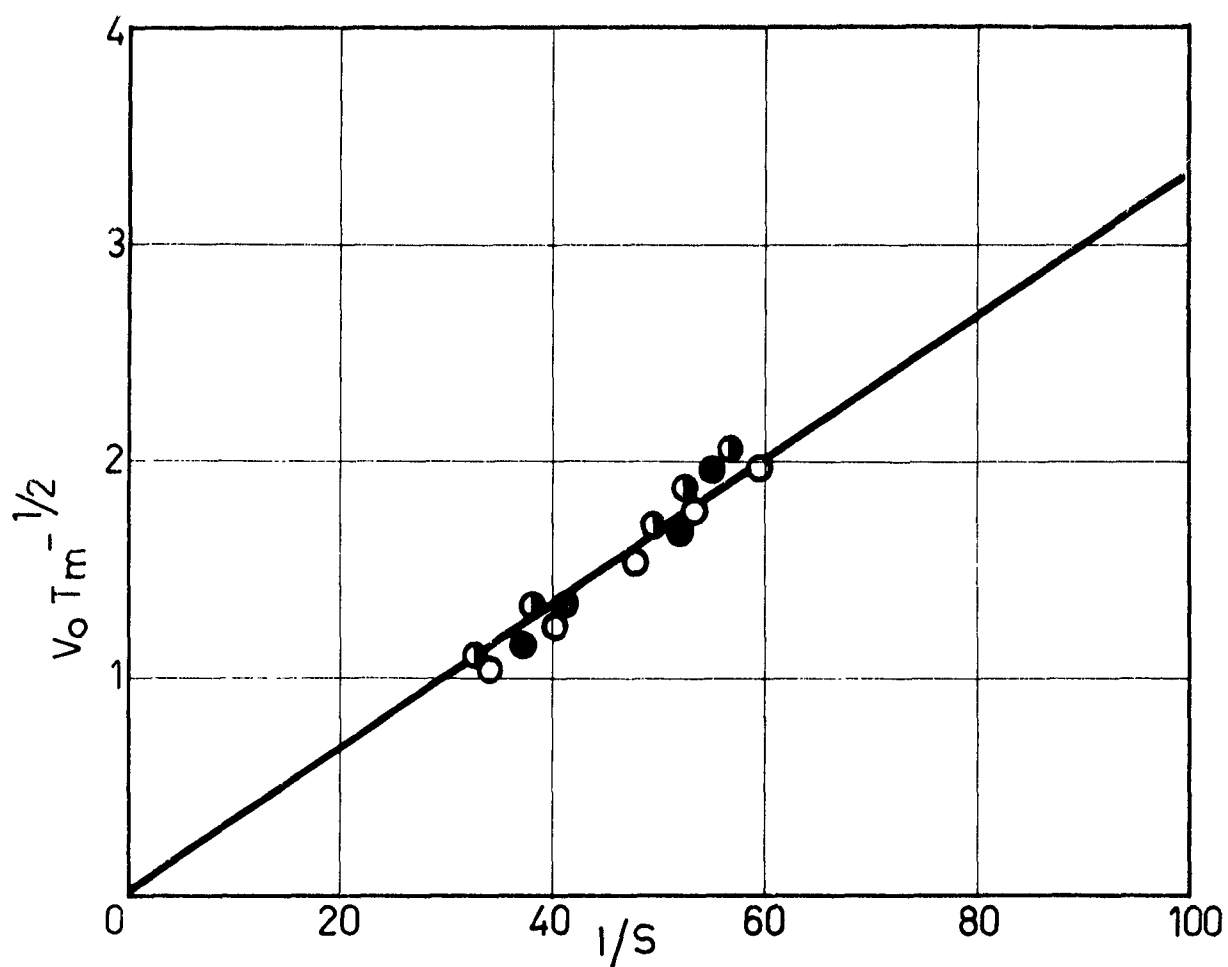
The results from experiments with unpreheated neopentane-oxygen-nitrogen mixtures are reported in Table 4. When these data are plotted in accordance with equation (5), as in Figure 8A, a straight line is obtained whose slope corresponds to an activation energy of 38.8 kcal mole<sup>-1</sup>.



ACTIVATION ENERGY OF NEOPENTANE-OXYGEN FLAMES  
FROM PREHEATING DATA

A :  $X=0.25$ ,  $E=36.5$ ,  $N_2 = 65\%$     B :  $X=0.15$ ,  $E=40.7$ ,  $N_2 = 67\%$   
 C :  $X=0.10$ ,  $E=40.1$ ,  $N_2 = 69\%$     D :  $X=0.05$ ,  $E=39.4$ ,  $N_2 = 71\%$   
 E :  $X=0$ ,  $E=39.9$ ,  $N_2 = 73\%$

FIGURE 6

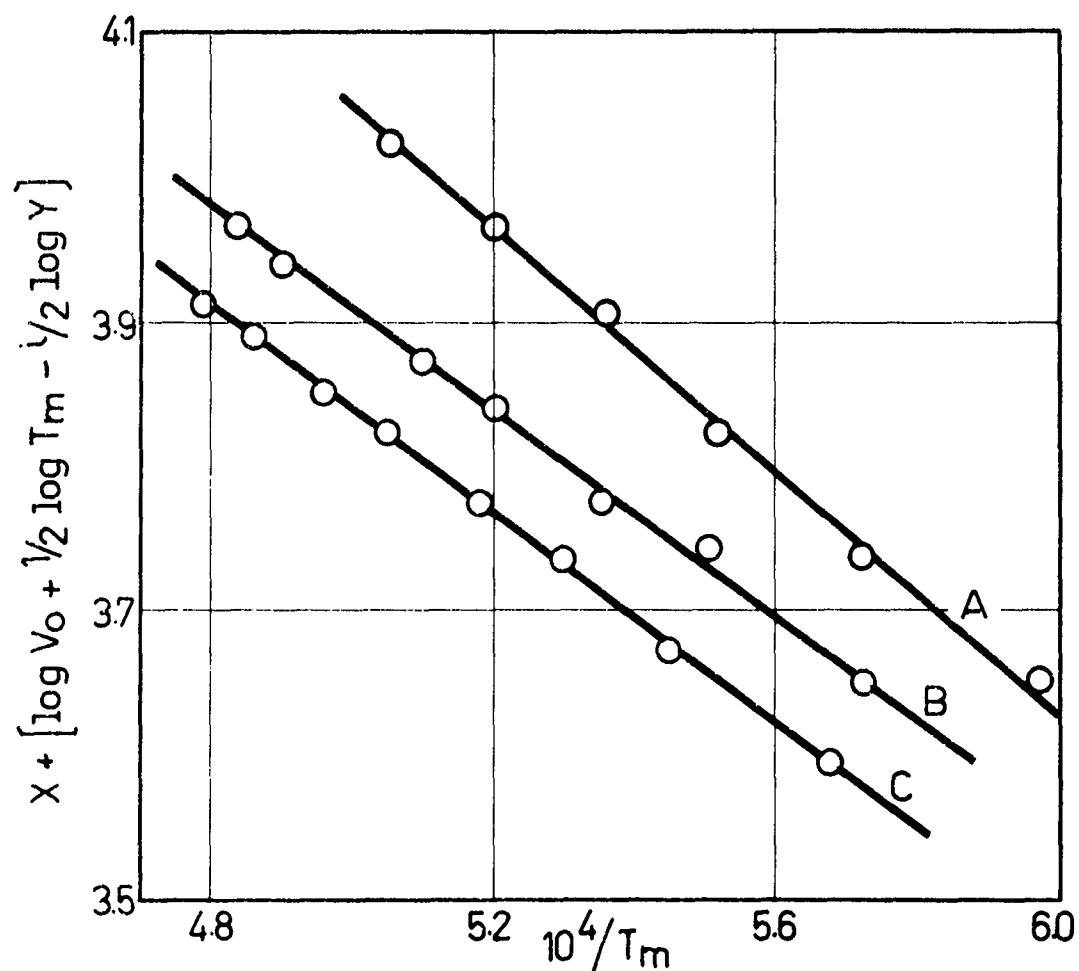


MEAN MOLECULAR WEIGHT OF CHAIN CARRIERS  
FOR NEOPENTANE-OXYGEN FLAMES

○,  $T_i = 290^\circ\text{K}$  ;    ◐,  $T_i = 300^\circ\text{K}$  ;    ●,  $T_i = 350^\circ\text{K}$  .

FIGURE 7.





ACTIVATION ENERGIES FROM DILUTIONS DATA,  $i=1$   
 A: NEOPENTANE - OXYGEN FLAMES,  $X=0.2$ ,  $R=0.111$ ,  $E=38.8$   
 B: n-BUTANE - OXYGEN FLAMES,  $X=0$ ,  $R=0.120$ ,  $E=32.7$   
 C: n-BUTANE - OXYGEN FLAMES,  $X=-0.05$ ,  $R=0.133$ ,  $E=33.3$

FIGURE 8.

TABLE 3

PREHEATED NEOPENTANE-OXYGEN-NITROGEN FLAMES; R = 0.111

$N_2$ %	$T_i$ °K	$T_f$ °K	$T_m$ °K	$V$ cm/sec	$S$ cm x 10 <sup>2</sup>
65	300	2569	1980	90	1.80
	355	2591	2009	95	-
	437	2607	2043	98	-
	530	2630	2085	108	-
	558	2642	2101	111	-
67	300	2490	1921	80	1.97
	354	2510	1957	85	1.84
	435	2533	1987	89	-
	524	2556	2027	99	-
	553	2563	2041	102	-
69	300	2423	1871	70	2.13
	352	2439	1896	71	1.97
	435	2462	1934	77	-
	520	2484	1974	84	-
	548	2495	1988	88	-
71	300	2333	1804	54	2.66
	347	2350	1830	57	2.46
	433	2378	1872	64	-
	512	2400	1909	69	-
	536	2411	1923	72	-
73	300	2260	1751	44	3.10
	344	2277	1774	48	2.66
	426	2300	1814	54	-
	501	2322	1849	58	-
	528	2328	1861	61	-

TABLE 4

UNPREHEATED NEOPENTANE-OXYGEN-NITROGEN FLAMES;  $R = 0.111$

$N_2$ %	$T_f$ $^{\circ}K$	$T_m$ $^{\circ}K$	$V_o$ cm/sec	$S$ cm $\times 10^2$
65	2568	1976	88	1.68
67	2495	1922	76	1.93
69	2422	1867	66	2.16
71	2333	1804	53	2.50
73	2266	1752	43	2.95
75	2165	1675	35	3.55

### 3. The n-butane-oxygen-nitrogen system

Only unpreheated mixtures containing n-butane were investigated; the data are presented in Table 5. For two fuel-oxidant ratios, the dilution by nitrogen was varied between 59 and 73 percent.

Plots of flame velocity,  $V_o$ , and the reciprocal intercone distance,  $1/S$ , against the fraction of flammable mixture are linear. Plots of the mean temperature,  $T_m$ , against  $Y$  are concave towards the concentration axis.

The data in Table 5 have been plotted according to equation (5) in Figure 8, curves B and C. The slopes of the resulting lines correspond to an activation energy of  $33.0 \pm 0.3$  kcal mole<sup>-1</sup>.

A plot of  $V_o / \sqrt{T_m}$  against  $1/S$  gives a common straight line for both fuel-oxidant ratios studied (Figure 9). The slope of this line yields a value of 23 for the mean molecular weight of the chain carriers.

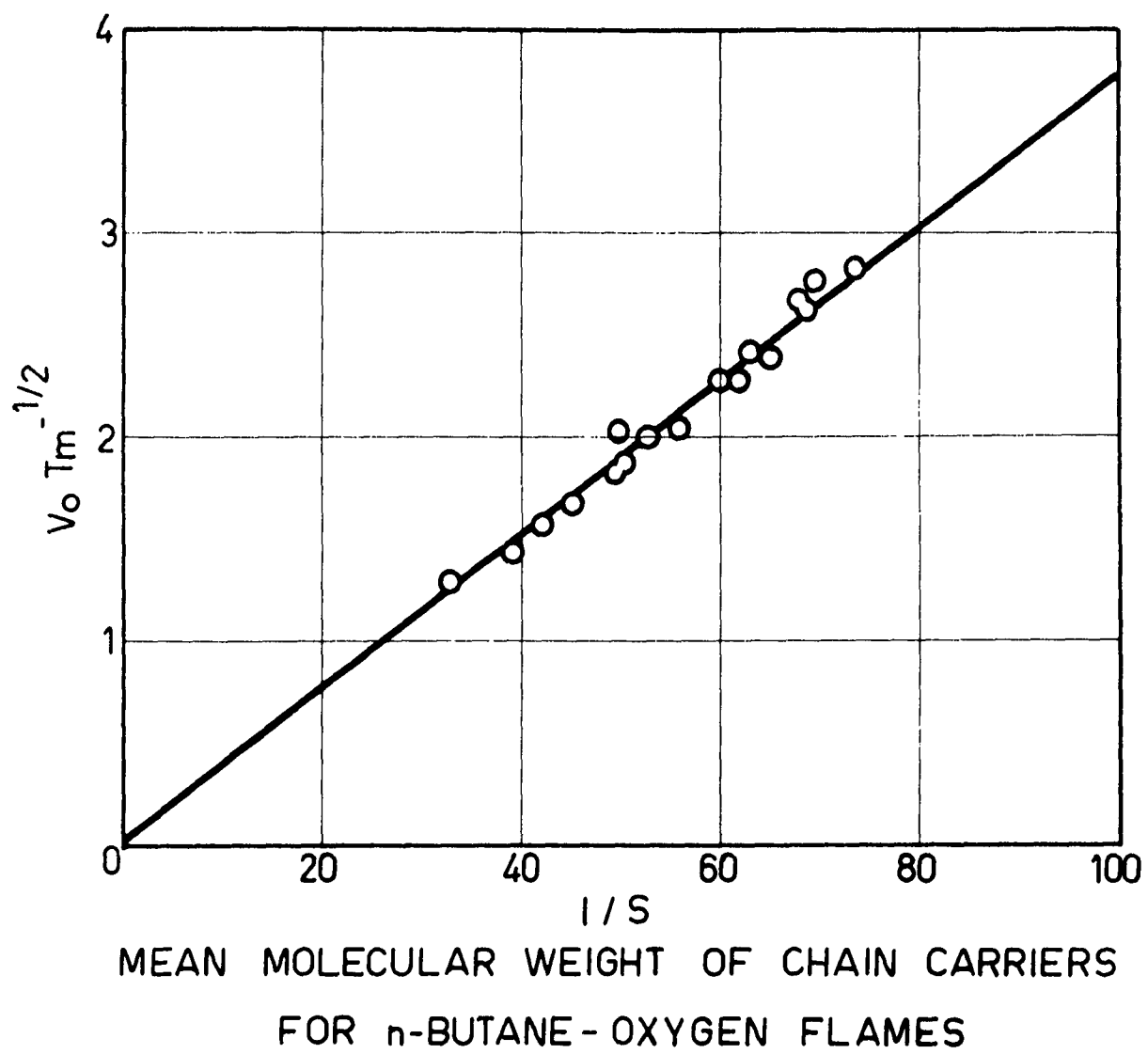


FIGURE 9

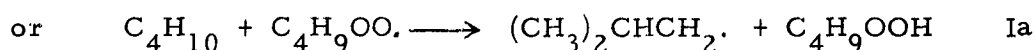
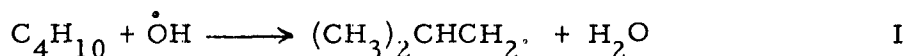
TABLE 5

## n-BUTANE-OXYGEN-NITROGEN FLAMES

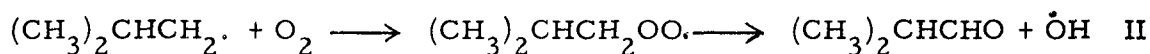
R	N <sub>2</sub> %	T <sub>f</sub> °K	T <sub>m</sub> °K	V <sub>o</sub> cm/sec	S cm x 10 <sup>2</sup>
0.120	59	2697	2068	130	1.36
	61	2659	2040	120	1.48
	63	2618	2010	108	1.51
	65	2551	1961	100	1.63
	67	2496	1920	90	1.74
	69	2423	1867	78	2.04
	71	2355	1817	71	2.26
	73	2262	1758	57	2.59
0.133	59	2720	2087	129	1.45
	61	2675	2055	120	1.49
	63	2623	2017	109	1.59
	65	2574	1983	100	1.70
	67	2511	1933	90	1.99
	69	2450	1888	79	-
	71	2378	1835	67	2.43
	73	2280	1760	56	3.00

## DISCUSSION

When the previously proposed mechanism<sup>2</sup> for the flame reaction is applied to isobutane-oxygen flames, two distinct possibilities exist, depending upon whether the isobutane is initially attacked at a primary or the tertiary position. Considering the propagation steps for attack on a primary H,

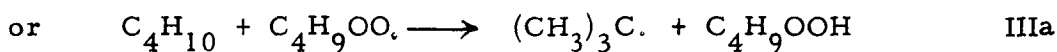
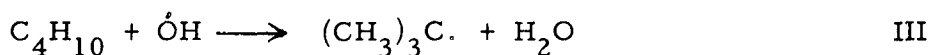


followed by

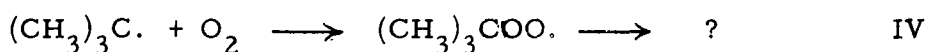


it is likely that the energy rich isobutylperoxy radical will dissociate rapidly into OH and isobutyraldehyde. Thus the chain may be considered to propagate alternately by isobutyl and OH radicals.

However, for tertiary attack, the propagating sequence is as follows :



followed by



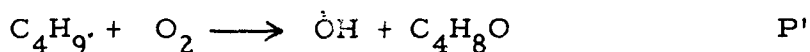
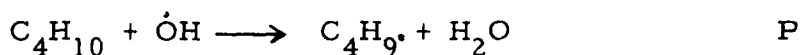
Tertiary butyl radicals may be considered to be one of the chain-carriers here, but the identity of the second is less clear. Tertiary butylperoxy radicals cannot undergo a simple decomposition to aldehyde and OH, analogous to reaction II. Therefore, if OH is to be accepted as the second chain carrying species, a decomposition yielding isobutene oxide or the biradical  $(\text{CH}_3)_2\underset{\cdot\text{CH}_2}{\overset{\cdot\text{C}}{\text{O}}}$  as coproduct with OH would have to take place.

Alternatively, the peroxy radical itself might be the second species to propagate the chain.

Falconer, Knox, and Trotman-Dickenson have shown<sup>11</sup> that in slow oxidations hydrocarbon attack at the tertiary position is eleven times as probable as that at a primary C-H bond at 350°C. They found no appreciable activation energy difference between the reactions at these two positions. If a similar preference for tertiary attack of isobutane by the chain propagating species, Y, is accepted for the flame reaction, then, due to the larger number of primary positions, reaction will follow the two paths I-II and III-IV in approximately equal proportions.

Two factors may thus contribute to the observed increase in molecular weight : (1) if the two proposed mechanisms together constitute the propagation reactions and alkylperoxy radicals are important as chain-carriers in one (or both) of the mechanisms, the large value of  $M_{C_4H_9OO}$  would tend to elevate the mean molecular weight of the chain carriers. (2) If  $C_4H_9$  has a reduced reaction efficiency due to possible steric hinderence in its subsequent reaction with oxygen, its lifetime would be increased, and the contribution of  $M_{C_4H_9}$  to the mean molecular weight would be greater than that of less hindered alkyl radicals.

If peroxy radicals are neglected on the grounds that their lifetimes are short compared with OH and alkyl radicals, the mechanism for propagation simplifies to



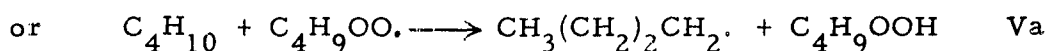
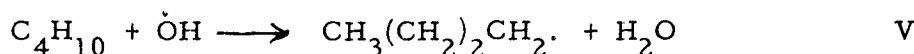
Then

$$\frac{\tau_{C_4H_9}}{\tau_{OH}} = f \frac{(C_4H_{10})}{(O_2)} e^{-\frac{(E_P - E_{P'})}{RT_m}} \quad (10)$$

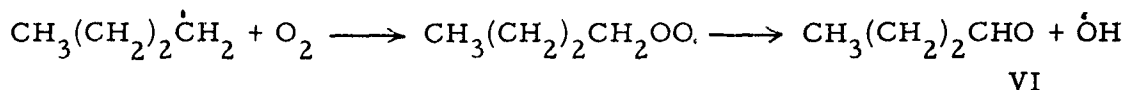
where f is the ratio of frequency factors for reactions of  $C_4H_9$  and OH radicals. Inserting the known value of M into equation (8),  $\tau_{C_4H_9}/\tau_{OH}$  is found to be 0.21. For the present series of experiments,  $(C_4H_{10})/(O_2)$

is 0.10 to 0.15, and  $T_m$  varies between 1530° and 2120°K.  $E_{p_1}$  is zero<sup>8</sup> to a good approximation, and  $E_p$  is about 6 kcal mole<sup>-1</sup> (ref. 7). Then  $f$  in equation (10) is found to be about 9. That is, the collision efficiency of reaction  $P'$  is about one-tenth that of reaction  $P$ . As the orientation for an effective collision between a small reactive radical, such as OH, with a hydrocarbon is not critical, reaction  $P$  should have a high collision efficiency. However, an alkyl radical, such as isobutyl, must have a more specific spacial orientation to undergo an addition reaction with oxygen. Therefore, the lower collision efficiency observed for reaction  $P'$  is in the expected direction. Any contribution of peroxy radicals to the mean molecular weight of 24 of the chain-carriers will necessarily lower  $\tau_{C_4H_9}/\tau_{OH}$ , and as a result, also lower the factor  $f$ .

For n-butane-oxygen flames, two possibilities again exist, as initial attack may be at a primary or secondary position. If a primary H is attacked, then

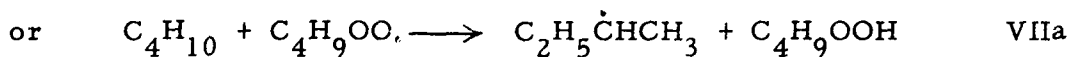
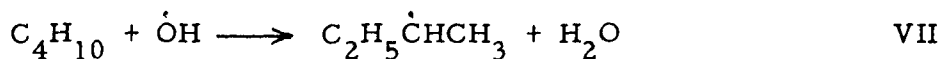


followed by

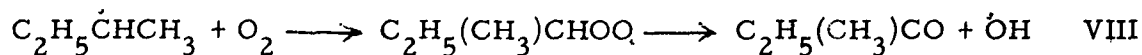


The energy rich butylperoxy radical formed in reaction VI will probably dissociate rapidly into OH and butyraldehyde, and the chain may be considered to propagate alternately by n-butyl and OH radicals.

If attack occurs at the secondary position, then



followed by :





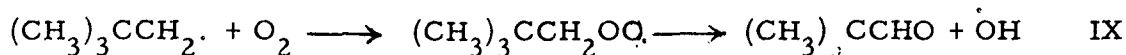
Here the secondary butylperoxy radical formed in reaction VIII will probably dissociate into OH and methylethylketone, and the chain thus propagates alternately by secondary butyl and OH radicals.

If secondary attack is accepted as being four times as probable as primary attack, as in slow oxidations<sup>11</sup>, then reactions will follow path VII-VIII about three times as often as path V-VI.

The observed mean molecular weight of 23 can be explained in the same manner as for isobutane-oxygen flames. Either butylperoxy radicals may be important in the chain propagation, or the collision efficiency of reactions VI and VIII may be less than that of reactions V and VII, or both factors may contribute. The enhanced stability of secondary butyl radicals over normal butyl radicals favours a longer lifetime for those radicals arising from secondary attack (tertiary butyl radicals should be again more stable).

If peroxy radicals are neglected as before, the relative collision efficiencies may be calculated. Inserting the value of  $M = 23$  into equation (8),  $\tau_{C_4H_9}/\tau_{OH}$  is found to be 0.18. From equation (10) a factor  $f$  of about 8 is found. These values are not unreasonable, for the same reasons as have been emphasized for the isobutane oxygen flame reaction. Again, any contribution from peroxy radicals will lower  $\tau_{C_4H_9}/\tau_{OH}$  and as a consequence lower  $f$ .

If neopentane undergoes an abstraction reaction similar to the butanes, only attack at primary C-H bonds is possible. The resulting neopentyl radical will not benefit from additional stabilisation as do secondary and tertiary butyl radicals. Thus it should react rapidly with oxygen to yield 2,2-dimethyl propionaldehyde and OH,



Peroxy radicals are no more likely to contribute to the mean molecular weight of the chain-carriers than in ethane flames, where the mean molecular weight is 17. Neopentyl radicals and OH may be considered to be

the alternate chain-carriers.

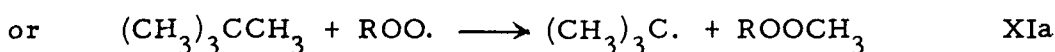
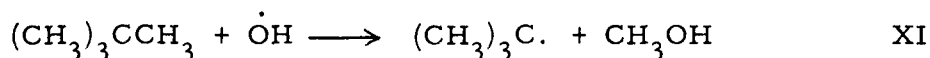
Knowing that  $M \approx 28$  for neopentane-oxygen flames,  $\tau_{C_5H_{11}}/\tau_{OH}$  is found from equation (8) to be 0.25. The ratio  $(C_5H_{12})/(O_2)$  is 0.125, and  $T_m$  is about 1800°K. Choosing  $(E_p - E_p^0) \approx 6$ , as before, then from equation (10),  $f$  is found to be about 11.

Thus the values of  $M$  observed for isobutane, n-butane, and neopentane can be explained by a sterically hindered reaction of the alkyl radical with oxygen. Alkylperoxy radicals, which may also contribute to the higher values found, need not have long lifetimes if the alkyl radicals themselves have lifetimes about one quarter of those of OH radicals.

If steric hinderence alone were insufficient to reduce the collision efficiency of reaction X,



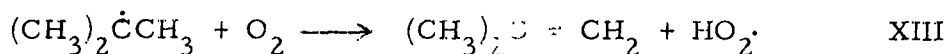
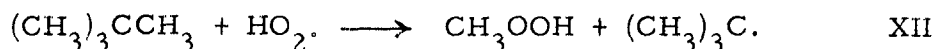
the factor  $f$  could also increase with increasing stability of the alkyl radical. Then  $f$  would be expected to be highest for isobutane, and lowest for neopentane, as the neopentyl radical is the least stable. However if an entire methyl radical is abstracted in neopentane attack,



then the more stable t-butyl radical will be formed. If reaction XI competes effectively with the normal hydrogen abstraction reaction to form neopentyl radicals, then the concentration of t-butyl radicals could be higher in neopentane flames than in isobutane flames. In isobutane, only one-half of the alkyl radicals are formed from tertiary attack; the remainder will be isobutyl radicals.

The previously observed<sup>11</sup> formation of isobutene as an initial product in the slow oxidation of neopentane cannot be explained in an analogous manner to the formation of olefins as first products in most paraffin oxidations.

The following reaction sequence is suggested :



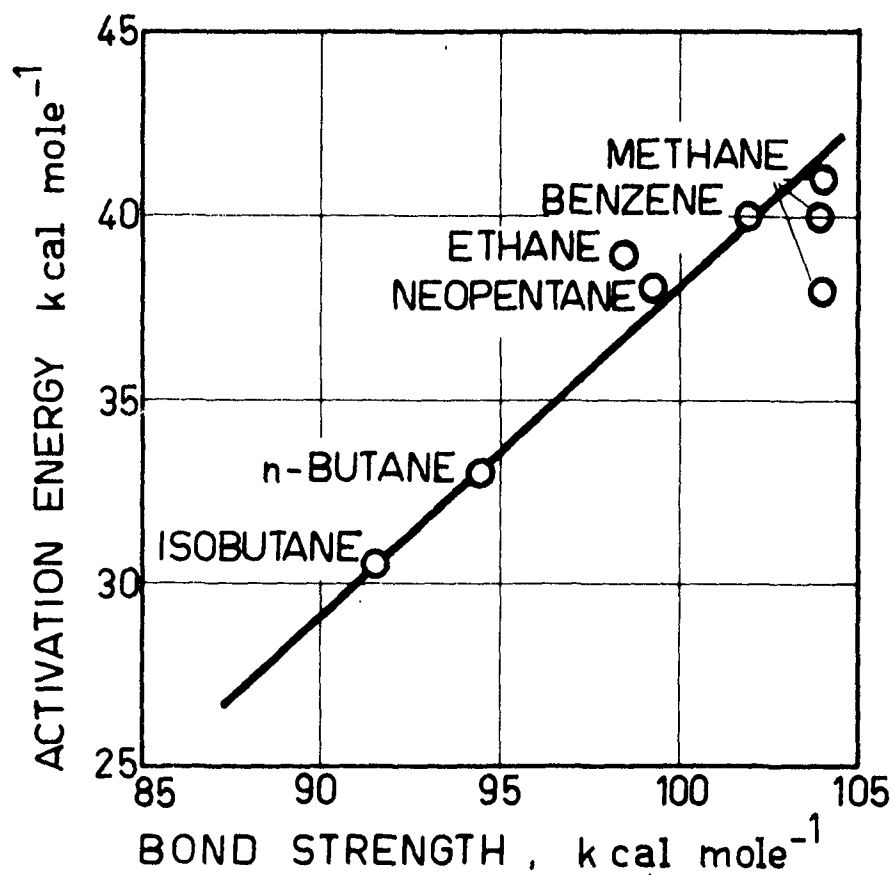
By analogy, reaction XI is not unreasonable.

The three possible explanations for the observed mean molecular weights of the chain propagating radicals in isobutane, n-butane, and neopentane flames burning in oxygen are then :

- 1) Steric hinderence may decrease the collision efficiency of alkyl radicals reacting with oxygen.
- 2) Alkyl radical stability increases with decreasing strength of the C-H bond broken to form the radical; more stable radicals should have longer lifetimes, and tertiary radicals should be able to contribute more to the value of M than secondary, and secondary more than primary.
- 3) The lifetimes of alkylperoxy radicals may be long enough to effectively increase M. The effect should increase with the stability of the alkylperoxy radical, which probably parallels that of the alkyl radical from which it is formed.

The present experiments do not enable a choice to be made from these possibilities.

The activation energies derived by the two methods explained in the introduction give values in excellent accord. Activation energies of 30.5, 33.0 and 38.3 kcal mole<sup>-1</sup> will be taken as representative for isobutane-, n-butane-, and neopentane-oxygen flames respectively. They are compared in Table 6 with overall activation energies of hydrocarbon-oxygen flames which have been investigated previously. It can be seen from Figure 10 that the activation energy for saturated hydrocarbon flames (diethylether and benzene flames can probably be included with those of alkanes in this grouping) decreases in an approximately linear fashion with the decreasing



DEPENDENCE OF ACTIVATION ENERGY  
UPON BOND STRENGTH OF WEAKEST C-H BOND

FIGURE 10

TABLE 6

ACTIVATION ENERGIES FOR HYDROCARBON-OXYGEN FLAMES

Hydrocarbon	Weakest C-H Bond kcal mole <sup>-1</sup>	Activation Energy kcal mole <sup>-1</sup>
Methane	103.9 (14)	38 (4), 40 (5), 41 (15)
Ethane	98.3 (14)	39 (5)
Neopentane	99.3 (14)	38.3
n-Butane	94.6 (14)	33
Isobutane	91.4 (14)	30.5
Diethylether	95-100 x	38.5 (10)
Benzene	101.8 (13)	40 (5)
Ethylene	102.5 (16), 105 (17)	36 (5)
Acetylene	121 (13)	32 (18, 19)
Hydrogen Sulfide	90 (13)	26 (10)

x This value for D(C-H) in diethylether appears reasonable in light of the similarities in the nature of reactions of ethers and of saturated hydrocarbons.

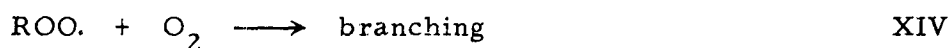
bond strength of the weakest carbon-hydrogen bond in the molecule. Ethylene and acetylene have activation energies much lower than this relationship would indicate.

The overall activation energy determined experimentally is principally that of the branching reaction, with smaller contributions from the alternating propagating reactions. The differences in activation energy of about 8 kcal mole<sup>-1</sup> observed between those saturated hydrocarbons containing only primary C-H bonds and isobutane, containing a tertiary C-H bond, cannot be attributed to differences in activation energies of the

propagating reaction alone because, for radical-hydrocarbon reactions where absolute activation energies are small, activation energy differences when the substrate molecules are changed are also small<sup>12</sup>. Therefore, the differences in activation energies must be assigned partly to the branching mechanism itself.

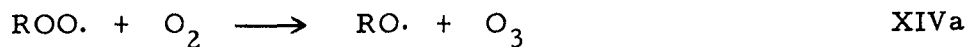
The observed parallelism between activation energy and bond strength suggests that those more stable radicals formed by the breaking of weak C-H bonds lead to a branching reaction with a lower activation energy in saturated hydrocarbon-oxygen flames, and that the activation energy is not greatly influenced by the molecular size. For unsaturated compounds, however, a reaction at the multiple bond must normally dictate the activation energy for subsequent branching. For an unsaturated hydrocarbon containing an easily abstracted hydrogen atom, as, for example, propylene, the reaction path having the lower activation energy would be expected to predominate the chain branching. Thus by extrapolating Figure 10, an activation energy of about 20 kcal mole<sup>-1</sup> might be expected for propylene, based on a carbon-hydrogen bond strength of 77 kcal mole<sup>-1</sup> in the paraffinic part of the molecule<sup>13</sup>.

The partial orders of 1.5 and - 0.5 for oxygen and isobutane, respectively, are identical to those previously found by Vandenabeele, Corbeels, and Van Tiggelen<sup>4</sup> for methane-oxygen flames. From the observed orders, it is clear that chain branching must occur between an oxygen molecule and a chain carrying radical that was also formed in a collision with oxygen. The most probable reaction<sup>4, 20, 21</sup> is one between the short lived energy rich alkylperoxy intermediate formed in reaction (X) and oxygen:



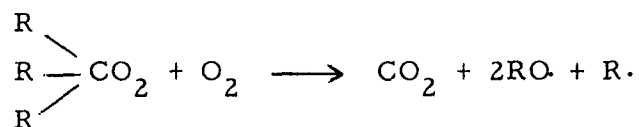
Although the exact form of reaction XIV is not easy to visualize, the reaction is certain to be highly exothermic, and this exothermicity coupled with the excess vibrational energy of formation possessed by the alkylperoxy

radical could overcome to a large extent unfavorable molecular rearrangement in the reaction. However, a reaction such as

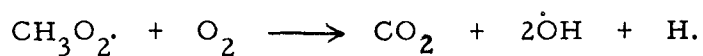


which has been proposed by Hanst and Calvert<sup>22</sup> for photosensitized hydrocarbon oxidations, provides branching with very little rearrangement.

As an alternative a possible branching reaction could be proposed according to the very general process :



where R. represents either any alkyl radical or even a single hydrogen atom as in the simplest case :



APPENDIXA STUDY OF ETHYLENE OXIDE-OXYGEN FLAMES.

The ethylene oxide-oxygen system is particularly interesting from the point of view of flame kinetics because ethylene oxide itself supports a decomposition flame. Therefore, in rich mixtures, the influence of this decomposition flame on the normal fuel-oxygen flame might be observed.

Considerable work which has been done on the mercury photosensitized<sup>23</sup>, photolytic<sup>24</sup>, and thermal<sup>25,26</sup> decompositions of ethylene oxide, enables certain generalizations to be made about the decomposition mechanism. An important role must be ascribed to the primary splitting into  $\dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{HO}$ , (reaction XV), followed by the rapid decomposition of the formyl radical (reaction XVI),



A lesser but important part may be played by reactions XVII and XVIII



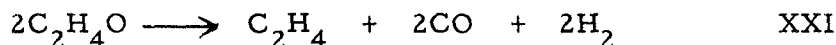
The evidence does not support the classical view of the decomposition into methylene radicals and formaldehyde,



Decomposition flames of ethylene oxide were first observed by Burden and Burgoyne<sup>27</sup>, and were later investigated by Gerstein et al<sup>28</sup> using a tube burner. Friedman and Burke<sup>29</sup> have stabilised ethylene oxide decomposition flames on a flat flame burner, and have found extremely low burning velocities (2.7 cm/sec at 1 atm. pressure). The experimental flame temperatures of about 1200°K are in excellent agreement with values



calculated by themselves and by Burden and Burgoyne<sup>27</sup>. These authors propose the simultaneous occurrence of the overall reactions



Despite the considerable interest shown in ethylene oxide reactions, a systematic study of its flames burning in oxygen has not, however, been reported.

In the burning velocity equation of the previously discussed theory for the propagation of stationary premixed flames<sup>1,2</sup>, two factors, the overall activation energy,  $E$ , and the mean molecular weight of the chain-carriers,  $M$ , are of particular interest when ethylene oxide-oxygen flames are considered.

Although no definite value has been found for the dissociation energy  $D(\text{C-H})$  of the carbon-hydrogen bond of ethylene oxide, it is generally accepted that this bond is paraffinic in nature, and a value of about 100 kcal mole<sup>-1</sup> is not in disagreement with this view. If this value is accepted, and the branching reaction is similar in nature to that for paraffinic hydrocarbons, an overall activation energy of about 39 kcal mole<sup>-1</sup> is expected (see Figure 10), at least for flames propagating in near stoichiometric flammable mixtures. As the oxygen content of the mixtures decreases, however, the activation energy might be anticipated to increase towards the 53 kcal mole<sup>-1</sup> found by Mueller and Walters<sup>26</sup> for the thermal decomposition of ethylene oxide, or the 65 kcal mole<sup>-1</sup> found by Burden and Burgoyne<sup>27</sup> from spontaneous ignition limits of ethylene oxide-air mixtures. Determination of the activation energy at different fuel-oxidant ratios should, therefore, throw light on the nature of the branching and propagating mechanisms.

For the wide variety of flames that have been studied<sup>3,6,10</sup>, the mean molecular weight of the chain propagating species has never been found to be less than 17. Even for hydrogen-oxygen flames, where one of the alternate chain carriers is probably a hydrogen atom, the lifetime of an H atom

in the presence of  $O_2$  is so short compared with OH that the value of M remains unchanged at 17.

The available information strongly suggests an abundance of hydrogen atoms and methyl radicals in ethylene oxide decomposition flames. In those ethylene oxide-oxygen flames in which oxygen is scarce, i. e. in very rich flames, the possibility arises that these light radicals can have enhanced lifetimes. If hydrogen atoms in particular are able to play an important role in chain propagation under these conditions, a marked decrease in the value of M should be observed. This effect should also be observed in the decomposition flames themselves, but, unfortunately, the flame structure of such slow burning flames renders impossible the measurement of the distance between the schlieren and luminous flame cones which is necessary for mean molecular weight determination<sup>29</sup>.

The present report discusses preliminary experiments performed with stoichiometric and lean ethylene oxide-oxygen mixtures, diluted with nitrogen. Flame temperatures, velocities, and distances between schlieren and luminous cones have been measured. Due to the interesting nature of these first results, the investigation is being continued to extend the present data into the rich flame region.

## EXPERIMENTAL

The experimental techniques were those described in the body of this report. Each value reported of the distance between schlieren and luminous cones is the mean of twelve measurements, reproducible to  $\pm 7\%$ .

Mixtures could not be preheated above 560°K because of prereaction; evidenced by the production of formaldehyde, at appreciably higher temperatures. At lower temperature, frequent tests indicated that no prereaction occurred.

All gases were commercial grade, purity about 99 %. Gas flows were measured on rotameters against a constant counter pressure of 4 cm Hg, to compensate for any resistance in the preheating tubes or in the burner itself. The flowmeter for ethylene oxide was calibrated by directing the effluent gas from the rotameter into the expendable inner chamber of an adapter designed, when used in conjunction with a standard wet test meter, to measure flows of water soluble gases<sup>30</sup>. The air expelled from the outer chamber of the adapter was measured by the wet test meter. Rotameters for oxygen and nitrogen were frequently calibrated directly against the standard wet test meter.

## RESULTS

### a. Preheated mixtures

Flame velocities, temperatures, and where possible, distances between schlieren and luminous cones have been measured for mixtures where  $R = \frac{(C_2H_4O)}{(C_2H_4O) + (O_2)}$  was 0.20 and 0.286, Y was 0.28 to 0.36, and  $T_1$  was varied between 300° and 560° K. The results are listed in Table 7.

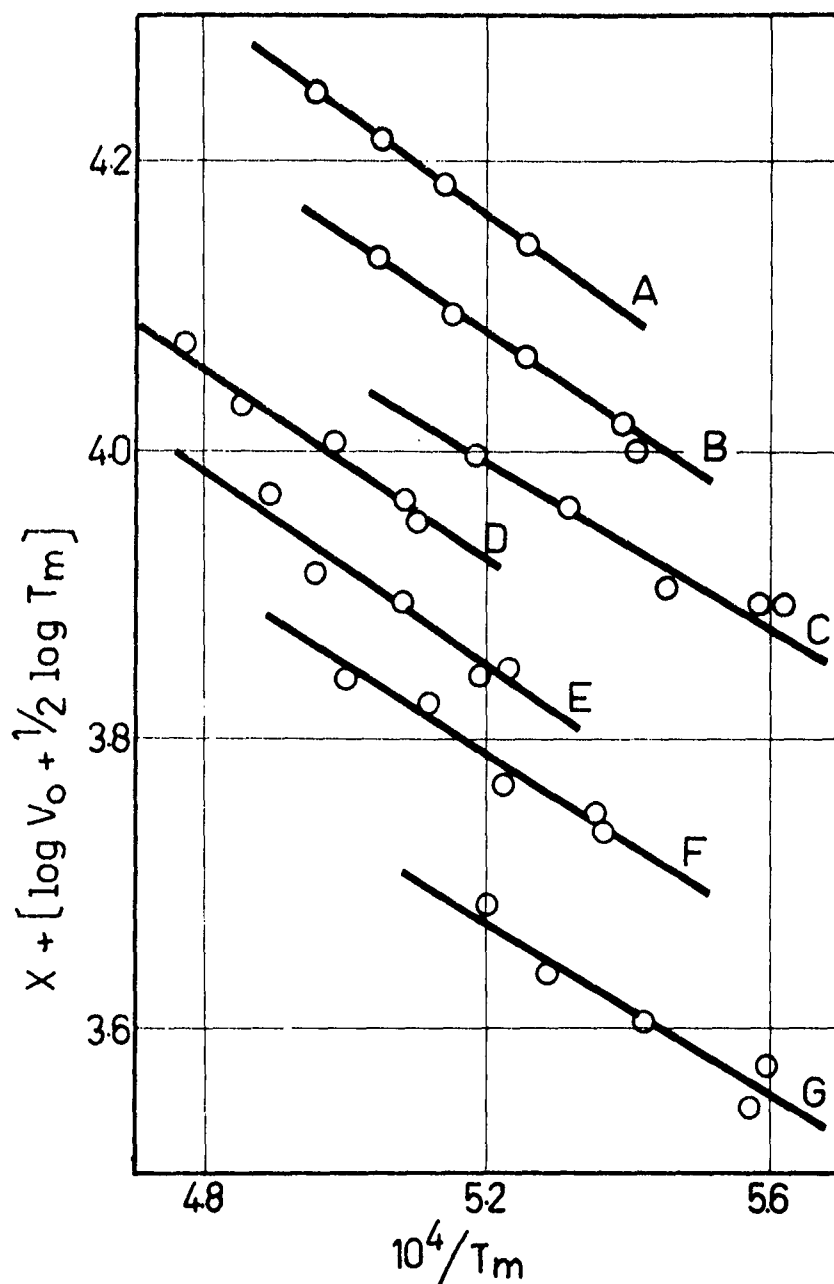
By plotting  $\log V_o + 1/2 \log T_m$  against  $1/T_m$  for these data, as in Figure 11, an activation energy of  $28.8 \pm 2.0$  kcal mole<sup>-1</sup> is found. By plotting  $\log V_o + 1/2 \log T_m - 1/2 \log Y$  against  $1/T_m$  (equation 5), as in Figure 12A, an activation energy of 29.2 kcal mole<sup>-1</sup> is found.

In Figure 13 a plot of  $V_o / \sqrt{T_m}$  against  $1/S$  has been made using the combined data from preheated and unpreheated gas mixtures. As predicted by theory, there is no significant difference in the mean molecular weight of the chain carriers when the initial gas temperature is changed. For stoichiometric mixtures, M was found to be 20, for lean mixtures ( $R = 0.20$ ), M was 27. As can be seen from Figure 13, however, these data are badly scattered, and considerable uncertainty must be attached to these values of M.

### b. Unpreheated mixtures

In Table 8 are presented results for flame velocity, temperature, and distance between schlieren and luminous cones obtained when R was 0.20 and 0.286 (lean and stoichiometric mixtures, respectively), and the nitrogen content was varied.

In Figure 12B,  $\log V_o + 1/2 \log T_m - 1/2 \log Y$  is plotted against  $1/T_m$  for the data for the two values of R investigated. A single straight line is found whose slope, independent of R, corresponds to an activation energy of 28.0 kcal mole<sup>-1</sup>.



ACTIVATION ENERGY OF ETHYLENE OXIDE-OXYGEN FLAMES FROM PREHEATING DATA

A:  $X=0.40$ ,  $R=0.200$ ,  $E = 31.2$ ,  $N_2 = 64 \%$

B:  $X=0.35$ ,  $R=0.200$ ,  $E = 29.7$ ,  $N_2 = 66 \%$

C:  $X=0.30$ ,  $R=0.200$ ,  $E = 25.8$ ,  $N_2 = 68 \%$

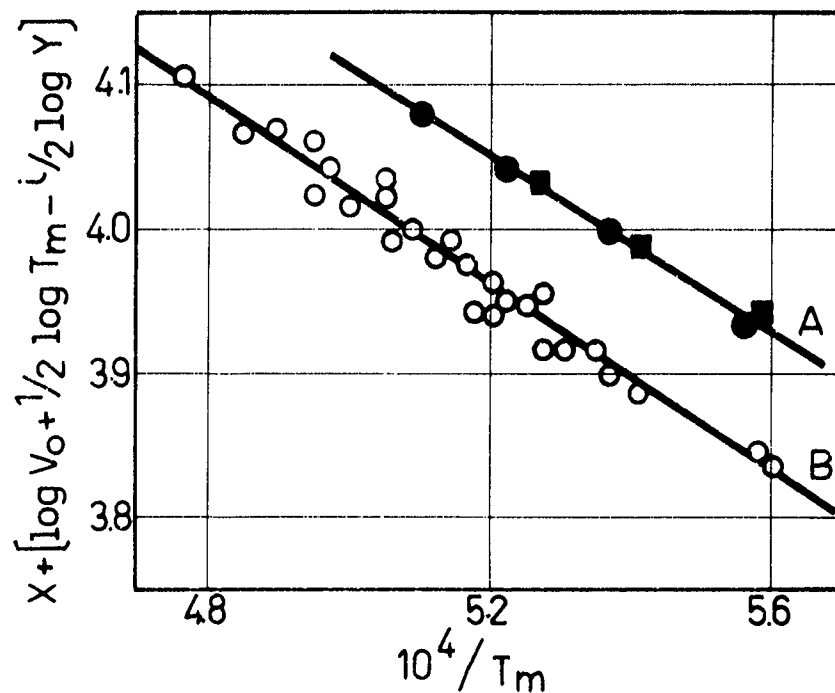
D:  $X=0.20$ ,  $R=0.286$ ,  $E = 30.8$ ,  $N_2 = 66 \%$

E:  $X=0.15$ ,  $R=0.286$ ,  $E = 30.4$ ,  $N_2 = 68 \%$

F:  $X=0.10$ ,  $R=0.286$ ,  $E = 27.2$ ,  $N_2 = 70 \%$

G:  $X=0$ ,  $R=0.286$ ,  $E = 26.6$ ,  $N_2 = 72 \%$

FIGURE 11.



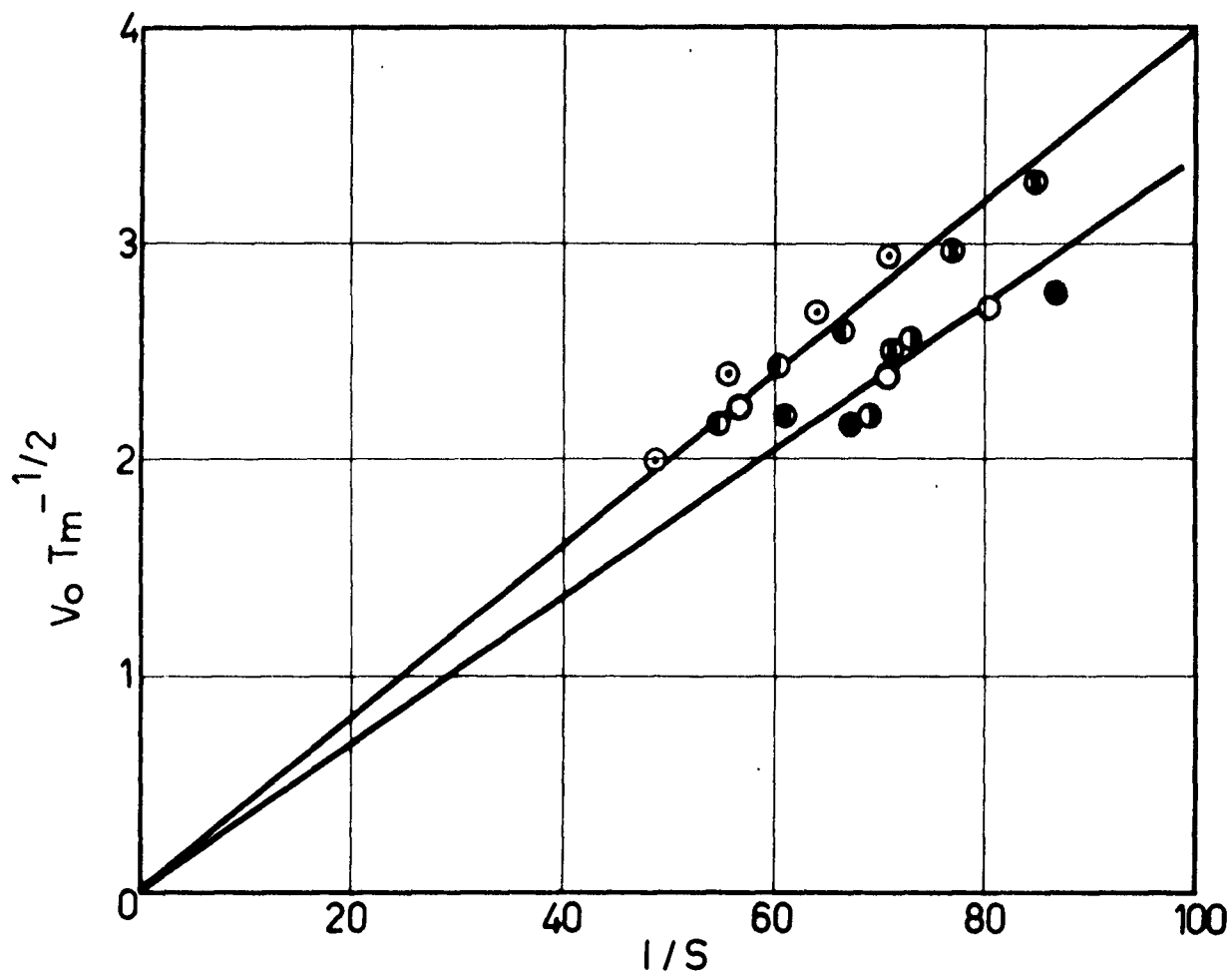
ACTIVATION ENERGY OF ETHYLENE-  
OXIDE - OXYGEN FLAMES

A: DILUTION DATA,  $X=0.1$ ,  $E=28.0$

●,  $R=0.286$  ; ■,  $R=0.200$

B: PREHEATING DATA USING DILUTION  
CALCULATION,  $X=0$ ,  $E=29.2$

FIGURE 12.



MEAN MOLECULAR WEIGHT OF CHAIN CARRIERS  
FOR ETHYLENE OXIDE-OXYGEN FLAMES

○  $R=0.200, T_i = 290^\circ\text{K}$  ; ●  $R=0.200, T_i = 300^\circ\text{K}$  ; ●  $R=0.200, T_i = 390^\circ\text{K}$ .

○  $R=0.286, T_i = 290^\circ\text{K}$  ; ●  $R=0.286, T_i = 300^\circ\text{K}$  ; ●  $R=0.286, T_i = 390^\circ\text{K}$ .

FIGURE 13

TABLE 7

PREHEATED ETHYLENE OXIDE-OXYGEN-NITROGEN FLAMES

R	N <sub>2</sub> %	T <sub>i</sub> °K	T <sub>f</sub> °K	T <sub>m</sub> °K	V cm/sec	S cmx10 <sup>2</sup>
0.20	64	300	2462	1902	125	-
		389	2495	1949	135	-
		470	2512	1982	145	-
		552	2535	2020	157	-
0.20	66	300	2400	1855	108	1.40
		389	2434	1902	118	1.15
		470	2457	1940	125	-
		553	2484	1982	138	-
0.20	68	300	2305	1783	93	1.47
		389	2339	1833	95	-
		473	2378	1883	106	-
		552	2406	1925	112	-
0.286	66	300	2552	1967	130	-
		389	2580	2011	143	1.22
		473	2618	2061	148	-
		556	2642	2099	164	-
0.286	68	300	2495	1925	112	1.51
		389	2524	1969	124	-
		473	2557	2017	130	1.34
		556	2568	2044	147	-
0.286	70	300	2423	1872	104	1.69
		389	2456	1919	109	1.41
		473	2473	1954	119	-
		553	2506	1999	123	-
0.286	72	300	2316	1790	88	1.87
		389	2350	1841	93	1.57
		470	2390	1891	99	-
		550	2406	1923	110	-



TABLE 8

## UNPREHEATED ETHYLENE OXIDE-OXYGEN-NITROGEN FLAMES

R	N <sub>2</sub> %	T <sub>f</sub> °K	T <sub>m</sub> °K	V <sub>o</sub> cm/sec	S cmx10 <sup>2</sup>
0.20	64	2466	1900	117	1.25
	66	2397	1850	104	1.42
	68	2317	1789	93	1.80
0.286	66	2552	1965	124	1.45
	68	2489	1918	115	1.60
	70	2417	1865	100	1.86
	72	2326	1797	83	2.10

## DISCUSSION

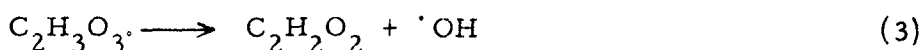
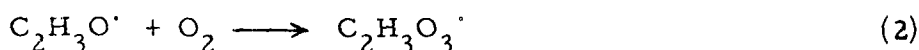
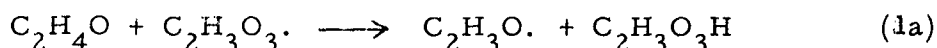
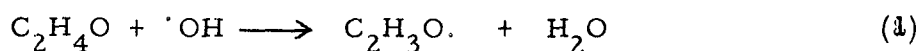
The fundamental kinetics of flames which propagate in stoichiometric or lean ethylene oxide-oxygen mixtures do not appear to be influenced by the decomposition reaction of ethylene oxide itself. The flame velocities and temperatures for flames burning in oxygen are evidently much higher than those that have been reported<sup>27-29</sup> for the decomposition flame. The overall activation energy of 28 kcal mole<sup>-1</sup> is only one-half of that determined by Mueller and Walters<sup>26</sup> for the thermal decomposition of ethylene oxide. Furthermore, the mean molecular weight of the chain-carriers is greater than 17 for both fuel-oxygen ratios studied, and hence does not indicate that either hydrogen atoms or methyl radicals, which would be expected from the decomposition, are important as chain propagating radicals in the combustion. The results thus suggest that ethylene oxide burns in oxygen by a branched chain mechanism similar to that responsible for the propagation of flames in other fuels.

The two methods used to determine the overall activation energy give values in excellent agreement; the mean value is 28.7 kcal mole<sup>-1</sup>. If the mechanism for ethylene oxide flames is similar to that for saturated hydrocarbons flames, this activation energy suggests that the dissociation energy  $D(C-H)$  of the first C-H bond in ethylene oxide is about 88 kcal mole<sup>-1</sup>. This value is rather low for a paraffinic C-H bond, and hence the low value of the activation energy may indicate that the branching mechanism is not identical to that for alkane-oxygen flames. In light of the uncertainty of the value for  $D(C-H)$ , further speculation on this point appears unprofitable.

It is not apparent why the mean molecular weight,  $M$ , of the chain carrying species should decrease from 27 for a lean mixture, ( $R = 0.20$ ), to 20 for a stoichiometric one. Despite the scatter in the experimental results, this difference is too marked to be dismissed as experimental error. Although the direction of change is that which is expected if the decomposition flame were increasingly to effect the combustion mechanism as the

fuel content of the flammable mixtures increased, it is unlikely that this effect would be noticable until considerable enrichment has occurred. A marked change would not be expected progressing from lean to stoichiometric mixtures. Furthermore, no corresponding change in activation energy is observed.

In chains that propagate alternately by OH radicals and a radical formed from the fuel molecule, the relatively long lifetime of OH gives a value of M, calculated from equation 1, very near to 17 for many fuels. Three possibilities exist as to why M is greater than 17 in ethylene oxide-oxygen flames : (i) If the chains propagated by the simple mechanism



and rate constant  $k_{1a}$  is not insignificant with respect to rate constant  $k_{10}$ , then a contribution from  $\text{M}_{\text{C}_2\text{H}_3\text{O}_3}$  will be responsible for an increase in M. (ii) If  $D(\text{C-H})$  for ethylene oxide is in fact as low as 88 kcal mole<sup>-1</sup>, the radical  $\text{C}_2\text{H}_3\text{O}\cdot$  will have an increased stability and its lifetime,

$\tau_{\text{C}_2\text{H}_3\text{O}}$ , may be long enough in comparison with that of its alternate, OH, to increase the mean molecular weight. The addition of oxygen to  $\text{C}_2\text{H}_3\text{O}$  (reaction (2)) may be less efficient due to steric effects than the abstraction reactions 1 and 1a, and the lifetime of  $\text{C}_2\text{H}_3\text{O}$  therefore increased. Thus any one of these factors individually, or any combination of them, could be responsible for the value of M observed for ethylene oxide oxygen flames.

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date : Februari 1962

by A. VAN TIGGELEN

Field : Chemistry

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Furthermore an estimation of the mean molecular weight of chain carriers can be derived from the values of the flame front thickness ; the values obtained give some information about the stability of the alkyl-radicals which are formed by hydrogen abstraction from the fuel molecule.

An appendix contains a similar study on the ethylene oxide-oxygen-nitrogen flames. There appears to be no essential difference between the burning of C<sub>2</sub> H<sub>4</sub> O and hydrocarbons : activation energy and molecular weight of chain carriers have quite normal values.

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